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1. REPORT DATE (DD-MM-YYYY) 30-05-2006		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Two Phase Transitions of Octa(ethylsilsesquioxane) (C ₂ H ₅ SiO _{1.5}) ₈ (PREPRINT)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Peter Müller, G. Poliskie, & K. Gleason (MIT); T. Haddad (ERC); R. Blanski (AFRL/PRSM)				5d. PROJECT NUMBER	
				5e. TASK NUMBER 23030521	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRSM 9 Antares Road Edwards AFB CA 93524-7401				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-JA-2006-179	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-JA-2006-179	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (AFRL-ERS-PAS-2006-133)					
13. SUPPLEMENTARY NOTES Submitted to Acta Crystallographica.					
14. ABSTRACT Crystals of the ethyl substituted octa-silsesquioxane (C ₂ H ₅ SiO _{1.5}) ₈ (ethyl POSS) undergo two phase transitions within the temperature range from 300K to 100K. At room temperature, crystalline ethyl POSS exhibits a plastic phase (phase I). When the temperature drops below about 255K, the molecular motion in the crystal slows to a rigid limit. This transition from phase I to phase II lowers the symmetry from rhombohedral to triclinic, corresponding to the change from one sixth of a molecule per asymmetric unit in the rhombohedral phase to half an independent molecule in phase II. In addition, this transition is fully reversible and is accompanied by the appearance (or disappearance when reversed) of threefold non-merohedral twinning. The second phase transition – from phase II to phase III – occurs around 240K and lowers the symmetry again: there are two half molecules per asymmetric unit in phase III, which is also triclinic. Even though the transition to phase III destroys the crystal, warming it to temperatures above 255K restores the plastic phase and the crystal “heals”.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Joseph M. Mabry
Unclassified	Unclassified	Unclassified	A	12	19b. TELEPHONE NUMBER (include area code) N/A

Two Phase Transitions of Octa(ethylsilsesquioxane) (C₂H₅SiO_{1.5})₈ (Preprint)

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Synopsis Crystal structures of the ethyl substituted octa-silsesquioxane (C₂H₅SiO_{1.5})₈ were determined at three different temperatures (260K, 250K and 100K). Two phase transitions were observed and are reported in this publication.

Abstract Crystals of the ethyl substituted octa-silsesquioxane (C₂H₅SiO_{1.5})₈ (ethyl POSS) undergo two phase transitions within the temperature range from 300K to 100K. At room temperature, crystalline ethyl POSS exhibits a plastic phase (phase I). When the temperature drops below about 255K, the molecular motion in the crystal slows to a rigid limit. This transition from phase I to phase II lowers the symmetry from rhombohedral to triclinic, corresponding to the change from one sixth of a molecule per asymmetric unit in the rhombohedral phase to half an independent molecule in phase II. In addition, this transition is fully reversible and is accompanied by the appearance (or disappearance when reversed) of threefold non-merohedral twinning. The second phase transition – from phase II to phase III – occurs around 240K and lowers the symmetry again: there are two half molecules per asymmetric unit in phase III, which is also triclinic. Even though the transition to phase III destroys the crystal, warming it to temperatures above 255K restores the plastic phase and the crystal “heals”.

Keywords: Polyhedral oligomeric silsesquioxane; Phase transitions; Plastic crystal; Non-merohedral twinning

1. Introduction

Many polyhedral oligomeric silsesquioxanes (POSS), cages of cyclic siloxanes with various organic substituents on the silicon atom, show plastic crystalline behavior and exhibit low-temperature phase transitions. Larsson (1960) crystallographically characterized several

POSS molecules and reported phase transitions for some of them. For example, for *n*-propyl POSS he reported a transition from hexagonal to triclinic symmetry at 272K. For some other species, including methyl, ethyl, *i*-propyl and *n*-butyl POSS, no phase transitions were reported, which may be due to the limited temperature range of Larsson's study. Kopesky *et al.* (2004) described a phase transition at 330K for *i*-butyl POSS by means of differential scanning calorimetry, and Poliskie *et al.* (2005) used differential scanning calorimetry, solid-state NMR spectroscopy as well as X-ray diffraction techniques to characterize two phase transitions in ethyl POSS. At the time of publishing their study, the X-ray diffraction data was of preliminary nature and was only sufficient for unit cell determination but had not given rise to satisfactory crystal structures. New data was collected and the crystal structures for three phases of ethyl POSS are reported in this publication. The claim of four distinct phases, as made in the abovementioned study, can no longer be sustained. The reported phases III and IV are in fact crystallographically identical and all differences in unit cell and density can be attributed to the different temperatures of data collection.

2. Experimental Details

Diffraction quality crystals were obtained by slow evaporation from tetrahydrofuran at room temperature. Diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), performing φ - and ω -scans. The diffractometer was equipped with a Cryo Stream 700 by Oxford Cryosystems, and complete data sets were collected at 260K (phase I), 250K (phase II), 230K and 100K (both phase III). Unit cell determinations for phase I were carried out using the diffractometer control software SMART version 5.6 (Chambers *et al.* 2003), and unit cells for the two low-temperature phases were determined with the help of the program CELL_NOW (Sheldrick 2005a). Data reduction for all datasets was performed with the program SAINT version 7.12 (Chambers 2005), and semi-empirical absorption correction was performed using SADABS (Sheldrick 2005b) or TWINABS (Sheldrick 2005c). All structures were solved by direct methods using SHELXS (Sheldrick 1990) and refined against F^2 on all data by full-matrix least squares with SHELXL-97 (Sheldrick 1997). All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Disordered ethyl groups in the structures of phases I and II were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters for the atoms involved. The

relative occupancies of the respective disordered components were refined freely, while constraining the total occupancy of both components to unity.

3. Results and Discussion

At temperatures above 255K (phase I), crystals of ethyl POSS give rise to a diffraction pattern with very broad spots that extends to only relatively low resolution: both a sharp drop in values for $I/\sigma(I)$ and a sharp rise of the merging R -values is observed between the resolution shells of 1.12 and 1.15 Å, and therefore the data was truncated at 1.13 Å. The diffraction pattern also shows significant non-Bragg background scattering (see Figure 1A), which suggests that large amounts of matter are in physical motion at room temperature, a description consistent with the definition of a plastic crystal. At temperatures between 255K and 240K (phase II) the diffraction pattern looks much different (see Figure 1B): the high background has vanished, the observable maximum resolution is much higher (0.84 Å) and the reflexes are sharper. In addition, the diffraction pattern appears to be that of a non-merohedral twin and a closer look at the crystal reveals the presence of several small cracks (see Figure 5B). When the temperature drops below 240K, (phase III) more changes can be observed: The maximum observable resolution decreases to about 0.9 Å and the maximum resolution to which complete data can be observed is even lower: only 92.4% completeness at $2\theta = 30^\circ$. The appearance of the diffraction pattern at 100K is consistent with a multiple non-merohedral twin and looks more like that of a sample not suitable for single-crystal X-ray analysis (see Figure 1C). Inspection of the crystal confirms that the second phase transition leads to multiple cracks, practically destroying the crystal (see Figure 5D). Further temperature decrease down to 100K does not cause any more changes in the appearance of the diffraction pattern, the size of the unit cell or the observed crystal structure. In fact, the two structures determined at 230K and 100K are perfectly isostructural, and only the 100K structure will be discussed as the crystal structure of phase III. All unit-cell parameters and other relevant crystal data for the three phases are given in Table 1.

Figure 1 Three frames of the same crystal of the ethyl-substituted POSS, taken in the same orientation, but at different temperatures. A: 260K (phase I, the plastic phase), B: 250K (phase II), C: 150K (phase III). The high amount of non-Bragg scattering visible at 260K disappears as the tumbling of the molecules slows to a rigid limit in phase II. At the same time, the resolution dramatically improves and the crystal splits into a threefold non-merohedral twin. The subsequent transition to

phase III causes severe crystal damage, leading to a drop in resolution.

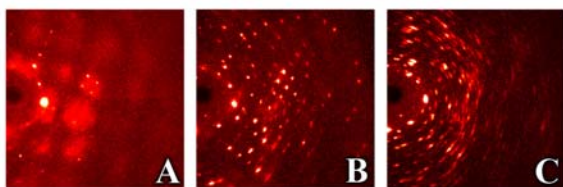


Table 1 Crystal data for the three phases of ethyl substituted POSS. For the rhombohedral phase I, both the primitive and the standard rhombohedral unit cell settings are given. This facilitates comparison between the unit cells of phases I and II.

	Phase I		Phase II	Phase III
Temperature [K]	260(2)		250(2)	100(2)
Space Group	$R\bar{3}$		$P\bar{1}$	$P\bar{1}$
Lattice setting	R -centered	Primitive	Primitive	Primitive
a [Å]	13.9747(4)	9.401	8.6125(17)	9.6067
b [Å]	13.9747(4)	9.401	9.6863(19)	12.138(2)
c [Å]	14.4729(10)	9.401	9.7112(19)	13.128(3)
α [°]	90	96.02	94.73(3)	87.68(3)
β [°]	90	96.02	96.83(3)	88.16(3)
γ [°]	120	96.02	98.69(3)	77.44(3)
Z	3	1	1	2
Z'	1/6		1/2	1
Calc. Density	1.321		1.363	1.445

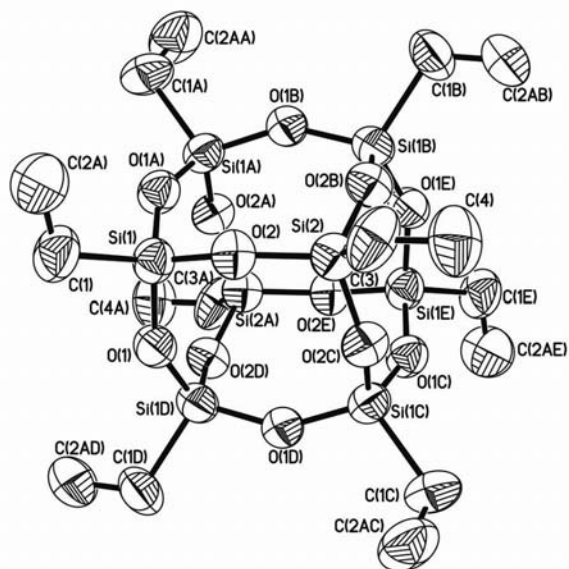
3.1. Phase I

IUCr The space group found for phase I is $R\bar{3}$, with a primitive rhombohedral unit cell of $a = b = c = 9.401$, $\alpha = \beta = \gamma = 96.02$. The asymmetric unit contains one sixth of a molecule, the remaining five sixths are generated by the crystallographic $\bar{3}$ axis. Both crystallographically independent ethyl groups are disordered, corresponding to a rotation about the C-C bond. One of these disorders involves the crystallographic threefold axis, which coincides with the C-C bond of the ethyl group in question. This threefold disorder has already been hypothesized by Larsson (1960) and can now be confirmed. The structure refines to very satisfactory residual values ($R1 = 0.0356$ for reflections with $I > 2\sigma(I)$ and $wR2 = 0.0989$ for all reflections), but a closer look reveals severely inflated thermal displacement parameters (the U_{eq} values of the non-hydrogen atoms range from 0.16 and 0.30). This can be attributed to two effects: First, limited tumbling of the molecule around a certain equilibrium orientation as described by the crystallographic model leads to large displacement ellipsoids owing to electronic delocalization. Second, entirely free and virtually unrestricted motion of

a portion of the molecules, without any preferred orientation at all is equivalent to a reduction of occupancy of the remaining at least somewhat ordered portion of molecules. Such a reduction in occupancy artificially increases the size of the thermal ellipsoids. In addition, fully unordered molecules in a crystal usually give rise to diffuse non-Bragg background scattering as is indeed observed (see Figure 1A). Most probably both effects are present in crystals of phase I, however the fact that the disorder of the ethyl group that is not on the crystallographic threefold axis can be resolved, leads to the assumption that the first effect may contribute less to the inflation of the thermal displacement parameters than the second one. Therefore, a bulk solvent correction was performed. Following Babinet's principle, SHELXL refines two parameters (Moews & Kretsinger, 1975). The first grows with the amount of diffuse solvent and usually possesses values around 1 when the mean electron density of the solvent and ordered parts of the structure is similar, as in most protein crystals. A large value of the second parameter indicates that only the low-angle data are influenced by the diffuse scattering of the bulk solvent; values of 2 to 5 are typical. In the case of freely tumbling ethyl POSS, the first parameter refined to 4.5, the second to 12, which indicates large regions of disordered matter of high mean electron density when compared to the rest of the structure, affecting most strongly the low-resolution data. Those values are atypical for bulk water in protein structures; they are, however, within a reasonable range for small molecule structures, where the chaotically disordered molecules contain atoms heavier than oxygen (Müller et al. 2001).

Figure 2 shows the molecular structure of the ethyl substituted POSS in phase I (at 260K) in a 15% ellipsoid representation. Even at this unusually low probability level, the ellipsoids seem large when compared to the structure of the same molecule in its phase II, based on data collected at 250K (Figure 3).

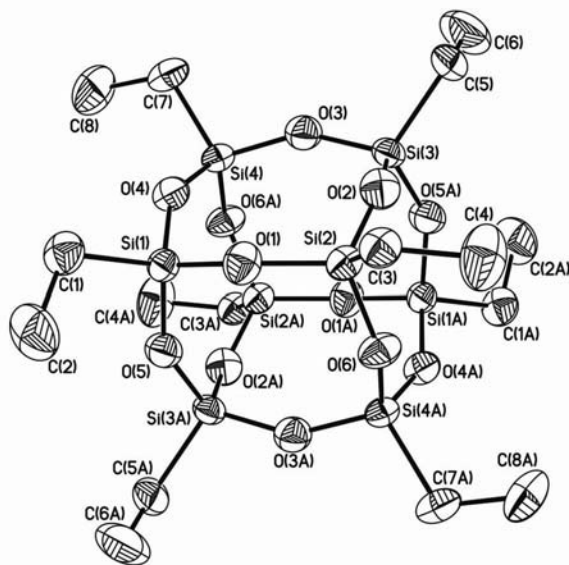
Figure 2 15% Probability ellipsoids of the 260K (phase I) structure of ethyl-POSS. For clarity, hydrogen atoms have been omitted and only the major components of the disorders are shown.



3.2. Phase II

Probably owing to slowing of the molecular motion in the crystal to a rigid limit at temperatures below 255K, the symmetry in the crystal is reduced in phase II. The three identical rhombohedral directions are no longer equivalent, changing the unit cell to the values reported in Table 1. The space group is $P\bar{1}$ with one half of a POSS molecule in the asymmetric unit, the second half is generated by the crystallographic inversion center. As the three directions were equivalent before the phase change, there are three different possible right-handed orientations of the new triclinic cell, corresponding to any of the three orthorhombic axes becoming a , b , or c of the triclinic cell. This is a description of a threefold non-merohedral twin, and all three theoretically expected domains are observed as three unit cells of the same dimensions rotated by approximately 120° from one another. The structure can be solved readily and, taking into account the twinning, refines well, giving rise to good residual values ($R1 = 0.0550$ for reflections with $I > 2\sigma(I)$ and $wR2 = 0.1482$ for all reflections). Besides threefold non-merohedral twinning and disorder of one of the four crystallographically independent ethyl groups, the crystal structure of phase II was a routine case.

Figure 3 50% Probability ellipsoids of the 250K (phase II) structure of ethyl-POSS. For clarity, hydrogen atoms have been omitted and only the major component of the disorder is shown.

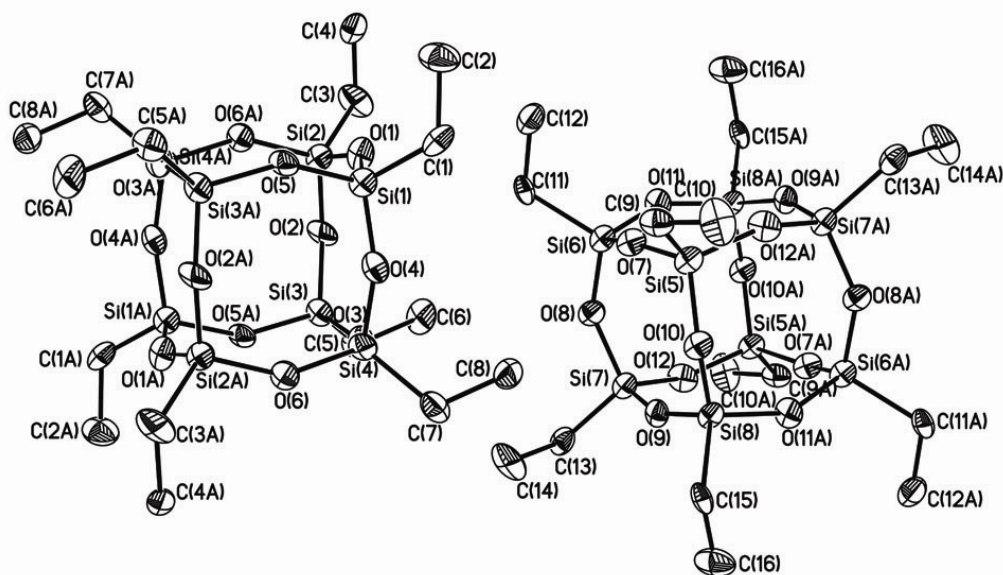


3.3. Phase III

Upon cooling to temperatures below 240K, a second phase transition occurs, again reducing the symmetry. The unit cell of phase III is triclinic – as the cell of phase II – but the asymmetric unit is doubled in size when compared to phase II, containing two half molecules. In addition the density of phase III is significantly higher than the densities of phase I and II, which are relatively similar (see Table 1). During the transition from phase II to III the crystal is fragmented even further and cracks heavily (see Figure 5D). Although a multitude of twin domains can be expected when a threefold non-merohedral twin cracks even further, 99% of the reflections observed can be explained with only four orientations of the same unit cell. However, the overall quality of the diffraction pattern and the maximum usable resolution are poor (see Figure 1C). Nevertheless a satisfactory structural model could be found and the final residual values are acceptable considering the quality of the data ($R1 = 0.0820$ for reflections with $I > 2\sigma(I)$ and $wR2 = 0.2489$ for all reflections).

Figure 4 50% Probability ellipsoids of the 100K (phase II) structure of ethyl-POSS. The figure shows both crystallographically independent molecules (the asymmetric unit contains two half

molecules). For clarity, hydrogen atoms have been omitted.



3.4. Comparison of the Three Phases

Larsson (1960) already described the correlation between phase-transition energy and the nature of the substituent on the silicon atom in different POSS species. He also speculated about a threefold disorder of one of the two independent alkyl groups in the plastic phase as a general feature of alkyl-POSS molecules at room temperature. This disorder is indeed found for the crystal structure of phase I of the ethyl substituted POSS and disappears during the transition to phase II. Interestingly, the twofold disorder of the other independent ethyl group in phase I is retained in phase II. No disorders can be resolved in phase III, nor are there any signs of unresolved disorder (such as elongated displacement ellipsoids or suspicious residual electron density maxima).

While it is not surprising that the packing of ethyl POSS becomes tighter with falling temperature it is interesting to note that the transition from phase I to II is accompanied with an increase in density that is barely significant, while phase III is significantly denser than phase II. This is in contrast to the observation that the structural changes are much larger during the transition from phase I to II, as are changes in other physical properties (Poliskie *et. al.*, 2006), when compared to the second transition. Another noteworthy feature of the ethyl POSS system is the change in intermolecular distances between the three phases: the shortest intermolecular methyl-methyl distance occurs in phase I, while the shortest intermolecular methyl-oxygen distance is found in the structure of phase III (see Table 2). This finding corroborates the assumption that the substituents on the POSS cage play a crucial role in the phase transition of this material.

Table 2 Shortest intermolecular methyl-carbon to methyl-carbon and methyl-carbon to oxygen distances for the three phases. The distances for phases I and II have been corrected for artefactual shortening due to libration following the method of Shomaker and Trueblood (1968), as implemented into the program XP (Sheldrick 1975).

Distances in Å	Phase I	Phase II	Phase III
Methyl-Methyl	3.38(4)	3.56(3)	3.75(2)
Methyl-Oxygen	4.11(2)	3.762(6)	3.449(17)

3.5. Reversibility of the Phase Transitions

Whenever there is a phase transition, the question of its reversibility is raised. Of the two distinguishable transitions, the one from phase I to phase II is accompanied by a stronger structural change. When characterized with other techniques (Poliskie *et. al.*, 2006), this transition has been found to be more prominent and, as mentioned above, corresponds to the slowing of the molecular tumbling to a rigid limit, thus making the lower limit of the plastic phase of ethyl POSS. To test for reversibility of this transition, a fresh crystal was mounted to the diffractometer at 260K and 160 frames were collected – sufficient information to determine a unit cell. The crystal was then slowly cooled to 250K and the measurement was repeated. Afterwards the temperature was raised back to 260K and the same 160 frames were collected again. Assuming reversibility, this corresponds to the following transitions: Phase I → Phase II → Phase I. In addition to the collecting of the 160 frames at each step, photographs of the crystal were also taken, as shown in Figure 5A-C. Despite the appearance of several small cracks and the formation of threefold non-merohedral twinning, the transition from phase I to II is fully reversible. Most of the small cracks disappear and the diffraction pattern of the crystal that was temporarily cooled to 250K is virtually indistinguishable from the pattern obtained before the cooling. Re-determination of the unit-cell is possible without problems, even although a little less straight forward than before the cooling and re-warming cycle, and leads to the same parameters.

To check the reversibility of the second phase transition, the same crystal was then cooled to 150K, which led to extensive cracking and the crystal became completely opaque (see Figure 5D). The 160 frames collected at this temperature looked as bad as the data previously obtained for phase III. Warming the crystal to 250K did not result in a change of the diffraction pattern and even though the crystal's clarity improved, most of the major cracks remained (see Figure 5E). This means the direct transition from phase III to phase II is not possible. Surprisingly, warming this badly cracked crystal to 250K caused an almost complete restoration of the original clarity (see Figure 5F), and the diffraction pattern once more looked like that of the fresh crystal. It should be pointed out, however, that this

succession of phase transitions ($I \rightarrow II \rightarrow I \rightarrow III \rightarrow I$) did do some damage to the crystal, as determination of the original rhombohedral unit cell from the last 160 frames was difficult. Figure 6 summarizes all possible transitions.

It can be theorized that the irreversibility of the transition from phase II to phase III is linked to the larger density gain when compared to the transition from phase I to phase II. The transition from phase I to phase II is determined by loss of molecular motion, which can simply be “switched on” again, figuratively speaking, by increasing the energy in the system, thus making this phase transition reversible. In contrast, the second phase transition is mostly driven by a gain in packing efficiency, and moderate increase in temperature cannot reverse this easily. When, however, the energy is increased to sufficiently high temperatures to allow for the molecular tumbling that is characteristic for phase I, the structural restraints of the more efficient packing in phase III can be overcome and the plastic phase is restored. This could be described as the molecules “knocking themselves into place” when the tumbling starts again.

Figure 5 Six pictures of the same crystal of ethyl-substituted POSS. A: A fresh, clear crystal at 260K (phase I). B: After cooling to 250K (phase II): some cracks are visible. C: Warmed again to 260K (phase I restored): most cracks have disappeared. D: After cooling to 150K (phase III): the crystal shows many cracks and is completely opaque. E: Warmed again to 250K: the crystal is still cracked but less opaque than at 150K. F: Warmed again to 260K (phase I restored): most cracks have disappeared.

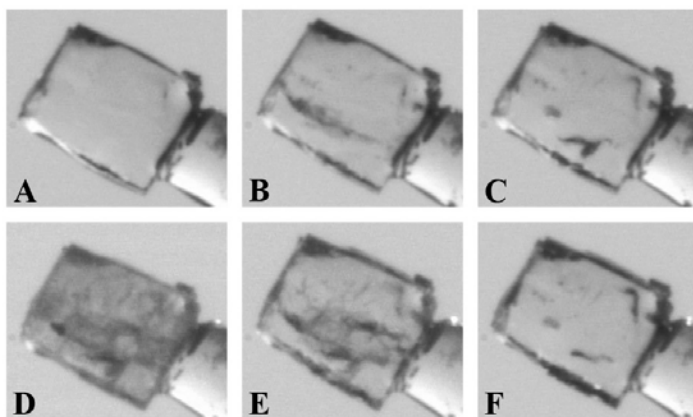
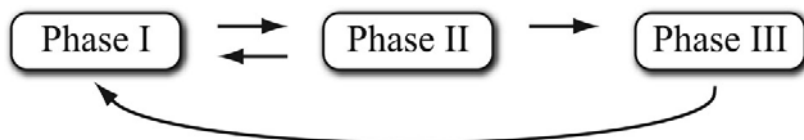


Figure 6 Summary of all possible phase transitions within the temperature range of 300K to 100K of ethyl POSS. The transition between phase I and phase II is fully reversible, while a transition from phase III to phase II could not be observed. However phase III can be transformed into phase I, which indirectly opens the way to phase II from phase III.



4. Conclusions

Ethyl substituted POSS shows two phase transitions within the temperature range examined (300K to 100K). The high temperature modification (phase I) was found to be a plastic phase of rhombohedral symmetry. Upon cooling below 255K the molecular motion in the crystal slows to a static limit, giving rise to a triclinic phase (phase II). This transition between phases I and II is fully reversible, although some minor defects remain in the crystal. During this phase transition, the unit cell dimensions, which are equivalent in the primitive rhombohedral unit cell of phase I become slightly different in the triclinic cell of phase II. This corresponds to the appearance (or disappearance when reversed) of threefold non-merohedral twinning. Below 240K, ethyl POSS forms another triclinic phase (phase III) of even lower symmetry. Although the transition from phase II to phase III destroys most of the crystal lattice and is irreversible, warming the crystal to temperatures above 260K restores the plastic phase and most cracks disappear.

Acknowledgements The authors acknowledge funding from the US Air Force under Grant No. F49620-01-1-0447.

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